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Polymer 40 (1999) 2103–2110

polymer

Crystal structure of the clathrate δ form of syndiotactic polystyrene containing 1,2-dichloroethane

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Received 24 June 1997; accepted 27 November 1997

Abstract

The crystal structure of the clathrate δ form of syndiotactic polystyrene containing 1,2-dichloroethane is presented. Polymer chains in **s**(2/1)2 helical conformation and 1,2-dichloroethane molecules are packed in the monoclinic unit cell with axes $a = 17.11$ Å, $b = 12.17$ Å, $c = 7.70$ Å and $\gamma = 120°$ according to the space group $P2_1/a$. The crystalline density of the clathrate δ form is 1.23 g cm^{-3} with two chains (eight monomer units) and two 1,2-dichloroethane molecules inside the unit cell. Molecules of 1,2-dichloroethane occupy isolated cavities between the benzene rings of adjacent polymer chains and are essentially only in the *trans* conformation. The location and the conformation of the 1,2-dichloroethane molecule are such that both chlorine atoms are sandwiched between two benzene rings of the same polymer chain.

Keywords: Syndiotactic polystyrene; Clathrate δ form containing 1,2-dichloroethane; Crystal structure

1. Introduction

Syndiotactic polystyrene (s-PS) presents a very complex polymorphic behaviour [1,2]. Four different crystalline forms have been described so far. The crystalline α and β forms are characterized by chains in the *trans* planar conformation, whereas the crystalline γ and δ forms are characterized by chains in the **s**(2/1)2 helical conformation. The crystal structures of the trigonal α form [3,4] and the orthorhombic β form [5–7] have been determined. Both α and β forms can exist in different modifications having different degrees of structural order, so that two limit disordered modifications (α' and β') and two limit ordered modifications (α'' and β'') have been described [3–6].

The term 'δ form' has been used to indicate different clathrate structures where helices of s-PS (the host) form a crystal lattice containing spaces in which molecules of a second chemical species (the guest) are located. For these clathrate structures the intensities and the precise locations of the reflections in the X-ray diffraction patterns change with the kind and the amount of the included guest molecules [1,8].

The clathrate δ form can be obtained by sorption of suitable compounds (e.g., methylene chloride, toluene, chloroform, etc.) in amorphous s-PS samples, as well as in semicrystalline s-PS samples being in the α or γ forms. The crystal structures of clathrate forms including molecules of toluene [9] and iodine [10] have been described.

By suitable extraction procedures, the clathrate δ form can be emptied and a crystalline form, free from guest molecules (δ_e form), can be obtained [11,12]. The crystal structure of the δ_e form has been described recently [13]. It is characterized by the presence of empty cavities which are occupied by guest molecules in the clathrate forms.

It is worth noting that the emptied clathrate form of s-PS (δ_e form) is different from the γ form, which can be obtained by thermal treatments of samples in the δ form, although both include only chains of s-PS in the helical **s**(2/1)2 conformation and do not include guest molecules.

Chatani et al. [9] have shown that clathrate δ forms containing similar organic compounds, e.g., toluene, benzene, chlorobenzene, *p*-xylene, are isomorphous. They have the same constants of the monoclinic unit cell, within experimental accuracy and the intensities of the reflections observed in the X-ray diffraction patterns of these clathrate forms were changed depending on the diffraction power of the guest. Chatani et al. [10] have also shown that a clathrate δ form of s-PS can be obtained with inorganic substances

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PII: S0032-3861(97)10372-X

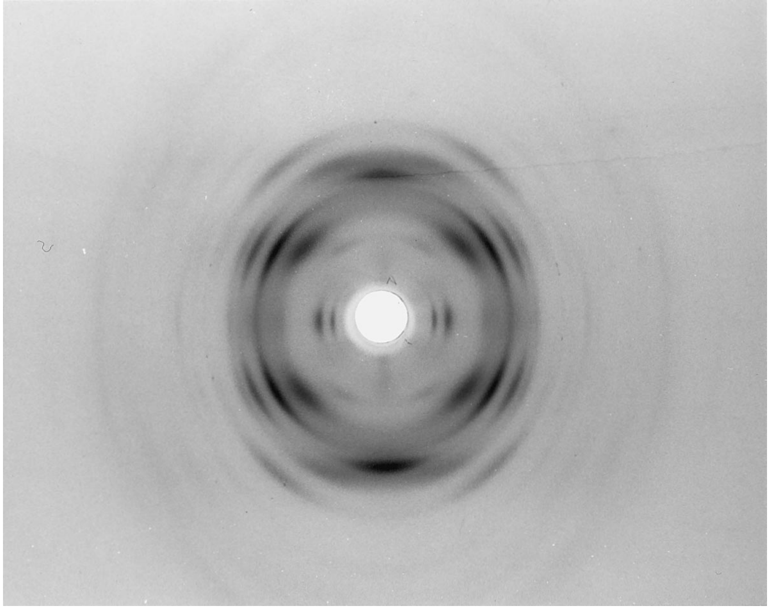

Fig. 1. X-ray fibre diffraction pattern of the clathrate δ form of s-PS containing DCE.

like, for instance, iodine. Also, the crystal structure of this clathrate form is isomorphous to that of the clathrate containing toluene [10].

It may be interesting to examine the possibility of formation of clathrate forms of s-PS where the guest is an organic compound which can assume different conformations. This provides a chance of studying the capability of the cavities in the clathrate forms of s-PS to induce particular conformations of the guest. Indeed, the shape and size-selectivity of s-PS in the absorption of specific organic substances can be used to separate solvent mixtures or to purify streams from traces of specific organic compounds [11].

The formation of a clathrate δ form of s-PS containing 1,2-dichloroethane (DCE) has been described recently [14]. The analysis of this clathrate form, through Fourier transform infrared spectroscopy (*FT*i.r.) [14], has shown that *trans* and *gauche* conformations of DCE molecules are nearly populated for the molecules absorbed in the amorphous s-PS. Indeed, the fraction of the *trans* conformation of DCE in the amorphous s-PS is 0.46, whereas DCE molecules absorbed in the crystalline phase, as guest molecules in the polymeric clathrate, are substantially only in the *trans* conformation [14].

In this paper the crystal structure of the clathrate δ form of s-PS containing DCE is presented and compared with the results of the *FT*i.r. analysis [14].

2. Experimental part and method of calculation

The s-PS was synthesized in our laboratories using a homogeneous catalyst consisting of $CpTiCl_3$ (Cp = cyclopentadienyl) and methylalumoxane (MAO) in toluene, according to the method described by Zambelli et al. [15]. The polymer fraction insoluble in acetone is 92%. The intrinsic viscosity of the fraction insoluble in acetone, determined in tetrahydronaphthalene at 135°C with an Ubbelohde viscosimeter, is 0.60 dl g^{-1}.

Oriented fibres in the δ clathrate form including DCE were obtained by exposing fibres in the α form to vapours of DCE. Fibres in the α form were obtained by stretching extruded samples of s-PS at 150°C.

The clathrate δ form of s-PS containing DCE transforms into pure helical forms of s-PS (γ and δ_e forms) by suitable treatments involving removal of the DCE molecules. Indeed, clathrate δ form samples are transformed into γ form by annealing at 130°C and into δ_e form by treatment with boiling acetone.

Wide-angle X-ray fibre diffraction patterns were obtained with nickel-filtered Cu Kα radiation and registered with a photographic cylindrical camera.

The thermogravimetric analyses were carried out with a Mettler TG50 Thermobalance in a flowing-nitrogen atmosphere at a heating rate of 10 K min^{-1}.

Calculated structure factors were obtained as $F_c = (\sum|F_i|^2 M_i)^{1/2}$, where M_i is the multiplicity factor and the summation is taken over all reflections included in the 2θ range of the corresponding diffraction spot observed in the X-ray fibre diffraction pattern. Only the values greater than the observable limit are reported. A thermal factor $B = 8$ Å^2 and atomic scattering factors from Cromer and Mann [16] were used. The observed structure factors F_o were evaluated from the intensities of the reflections observed in the X-ray fibre diffraction pattern, $F_o = (I_o/LP)^{1/2}$, where LP is the Lorentz-polarization factor for X-ray fibre diffraction: $LP = (1 + \cos^2 2\theta)/[2(\sin^2 2\theta - \zeta^2)^{1/2}]$, with $\zeta = \lambda l/c$, l

Table 1
Diffraction angles 2θ, Bragg distances d, reciprocal coordinates ξ and ζ of the reflections observed on the layer lines l in the X-ray fibre diffraction pattern of the clathrate δ form of s-PS containing DCE of Fig. 1

2θ (deg)	d (Å)	ξ (Å^{-1})	ζ (Å^{-1})	l
8.50	10.4	0.096	0	0
10.75	8.23	0.121	0	0
17.0	5.21	0.192	0	0
21.0	4.23	0.236	0	0
25.5	3.49	0.286	0	0
33.6	2.67	0.375	0	0
35.6	2.52	0.397	0	0
13.7	6.45	0.085	0.130	1
17.5	5.07	0.149	0.130	1
21.3	4.18	0.201	0.130	1
24.3	3.67	0.240	0.130	1
26.5	3.37	0.267	0.130	1
30.0	2.98	0.310	0.130	1
23.0	3.87	0	0.259	2
25.5	3.49	0.121	0.259	2
29.3	3.04	0.202	0.259	2

and c being the order of the layer line and the chain axis, respectively. The experimental intensities I_0 were observed by the multiple-film method and measured visually with an intensity scale.

The packing energy of the s-PS chains only was evaluated as half the sum of the interaction energies between the atoms of one monomeric unit and all the surrounding atoms of the neighbouring macromolecules. The packing energy of the guest DCE molecule in the cavity was calculated as half the sum of the interaction energies between the atoms of the DCE molecule and all the atoms of the neighbouring s-PS chains which delimit the cavity. The interactions were calculated within spheres of radii equal to twice the sum of the van der Waals radii for each pair of atoms. The conformation of the chains, and hence the c axis, was kept constant in the calculations. The chain conformation is that found in the crystal structure of the δ_e form of s-PS [13]. The bond angle on the methine carbon atoms is 111.8°, whereas those on the two methylene carbon atoms belonging to two successive monomeric units are 115.8° and 116.8°; the two torsion angles, for the **s**(2/1)2 helical symmetry, are 180.1° and 63.2°. The packing energy calculations were performed using non-bonded energy functions with the constants reported by Flory and coworkers [17]. The parameters involving chlorine atoms have been derived according to the procedure of Suter and Flory [18] and Brant et al. [19] from the basic data of Ketelaar [20] (polarizability and van der Waals radius) and Hopfinger [21] (effective number of electrons).

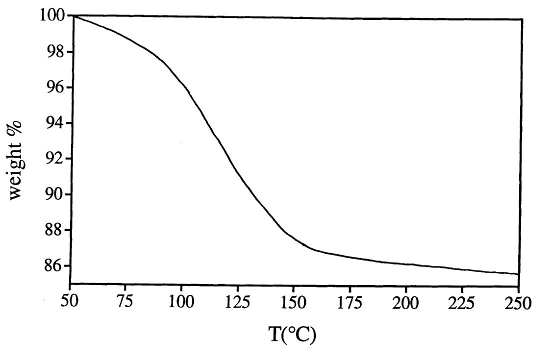

Fig. 2. Thermogravimetric measurement for a powder sample of clathrate δ form containing DCE.

3. Results and discussion

The X-ray fibre diffraction pattern of the clathrate δ form of s-PS with DCE is reported in Fig. 1. All the reflections observed in the fibre pattern are listed in Table 1. The reflections were indexed in terms of a monoclinic unit cell with cell constants $a = 17.11 \pm 0.06$ Å, $b = 12.17 \pm 0.06$ Å, $c = 7.70 \pm 0.06$ Å, $\gamma = 120.0 \pm 0.5°$. In addition, the 002 meridional reflection was observed in the tilted pattern. The space group is $P2_1/a$, in agreement with the systematic absence of $hk0$ reflections with $h = 2n + 1$ and $00l$ reflections with $l = 2n + 1$.

Thermogravimetric measurements indicate weight losses in the range 10–14%. Indeed, the amount of guest molecules included in the crystalline structure is dependent on the sorption as well as desorption (and storage) conditions. A thermogravimetric scan for a powder sample of clathrate δ form with DCE, showing a weight loss of 14%, is reported, as an example, in Fig. 2. Based on this data, on the space group and on the size of the cavities formed between the polymer chains, the molar ratio of monomer/DCE was assumed to be 4/1. The calculated density is 1.23 g cm^{-3} for the unit cell containing two chains of s-PS in the helical **s**(2/1)2 conformation (eight monomer units) and two DCE molecules. This is comparable with the experimental density of 1.12 g cm^{-3} measured by flotation on a sample with a crystallinity of $\approx 40\%$.

It is worth noting that the space group is the same as that found for the structure of the clathrate δ form containing toluene [9]. Moreover, the dimensions of the unit cells are very similar in these two clathrate δ forms. This suggests a similar structural model for the two clathrates, at least as far as the positioning of the polymer chains is concerned. The s-PS chain was positioned in the unit cell with its twofold screw axis coincident with the crystallographic twofold screw axis in the space group $P2_1/a$ at $x = 0.25$, $y = 0$. In order to find the best orientation of the s-PS chains around their axes, calculations of the packing energy were performed for the space group $P2_1/a$.

At first the packing energy of the s-PS chains only, i.e., without the guest molecules, was calculated whilst keeping the axes of the unit cell constant and varying the orientation of the chain around its axis (represented by the angle ω defined in Fig. 3) and the z coordinate that defines the relative heights of the chains in the unit cell. A map of the

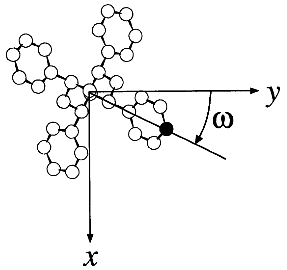

Fig. 3. Definition of the variables used in the packing energy calculations of the s-PS chains only. ω is the angle of rotation of the **s**(2/1)2 helical chain of s-PS around the chain axis; it is positive for a clockwise rotation. The height of the carbon atom indicated by a filled circle defines the coordinate z (Å).

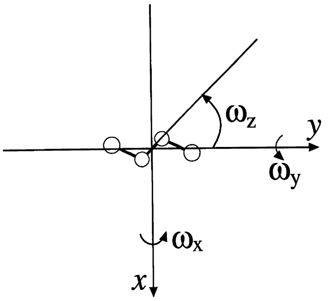

Fig. 5. Angles of rotation ω_x, ω_y and ω_z which define the orientation of the DCE molecule inside the unit cell. The values of ω_x, ω_y and ω_z are positive for a counter-clockwise rotation.

packing energy as a function of ω and z for the space group $P2_1/a$ is reported in Fig. 4. The map is periodic over $\omega = 180°$ and $z = c/2$; therefore, only the portion of the map in the range $\omega = 0$–$180°$ and $z = 0 - c/2$ is shown. The map presents two different energy minima. Only for the absolute minimum ($\omega = 165°$, $z = 2.90$ Å) are the chains of s-PS arranged so that there is plenty of space for including the guest DCE molecules. As expected, the orientation of the chains is nearly the same as that found in the crystal structure of the emptied clathrate δ form (δ_e form) [13] or in the structures of the clathrate δ forms containing toluene [9] or iodine [10]. As in the structure of the clathrate with toluene [9], there are isolated holes between the polymer chains centred at the centres of symmetry of the lattice.

We first assumed that DCE molecules in the cavities were in *trans* conformation, as suggested by *FT*i.r. analysis [14]. The DCE molecule can be disposed with the centre of the C–C bond coincident with the centre of symmetry at $x = y = 0.5$. The best orientation of the DCE molecules inside the unit cell was found by calculations of the packing energy of the guest DCE molecule in the cavity. The calculations were performed by maintaining the orientation of the s-PS chains constant, as in the position of the absolute energy minimum of the map of Fig. 4, and varying the orientation of the DCE molecule around the three orthogonal axes x, y and z, having the origin coincident with the centre of the C–C bond (hence coincident with the centre of symmetry). The orientation of the DCE molecule is represented by the three angles ω_x, ω_y and ω_z, defined in Fig. 5; if $\omega_x = \omega_y = 0$ then the plane containing the atoms Cl–C–C–Cl of DCE in *trans* conformation is parallel to the *ab* plane of the unit cell.

Two maps of the packing energy as a function of ω_y and ω_x, and as a function of ω_z and ω_x for the DCE molecules in

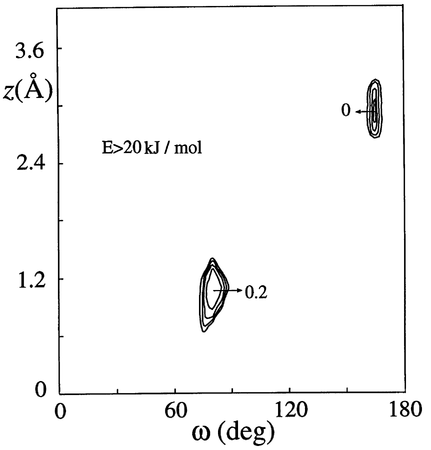

Fig. 4. Map of the packing energy of s-PS chains without the guest molecules as a function of ω and z for the space group $P2_1/a$. The curves are drawn at intervals of 5 kJ/(mol monomer unit) with respect to the absolute minimum of the map assumed as zero.

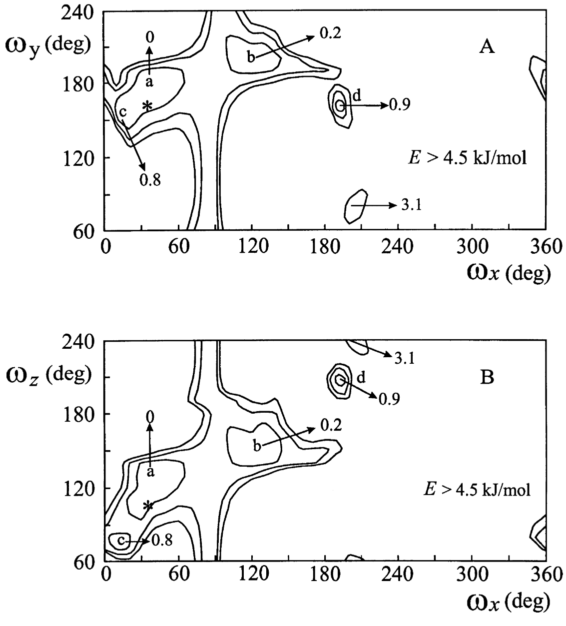

Fig. 6. Maps of the packing energy of the DCE molecule in the cavity as a function of ω_y and ω_x (A) and as a function of ω_z and ω_x (B), for the space group $P2_1/a$. All angles are varied in steps of 5°. For each pair (ω_y, ω_x) (A) or (ω_z, ω_x) (B), the third angle, ω_z (A) or ω_y (B), is varied and the minimum energy value is reported. The curves are drawn at intervals of 1.5 kJ/(mol of DCE molecule) with respect to the absolute minimum of the map assumed as zero. The energy minima are indicated by the letters a, b, c and d. Values of the energies of the minima are also indicated. The final model which give the best agreement between calculated and observed X-ray intensities is indicated with an asterisk ($\omega_x = 35°$, $\omega_y = 160°$, $\omega_z = 105°$).

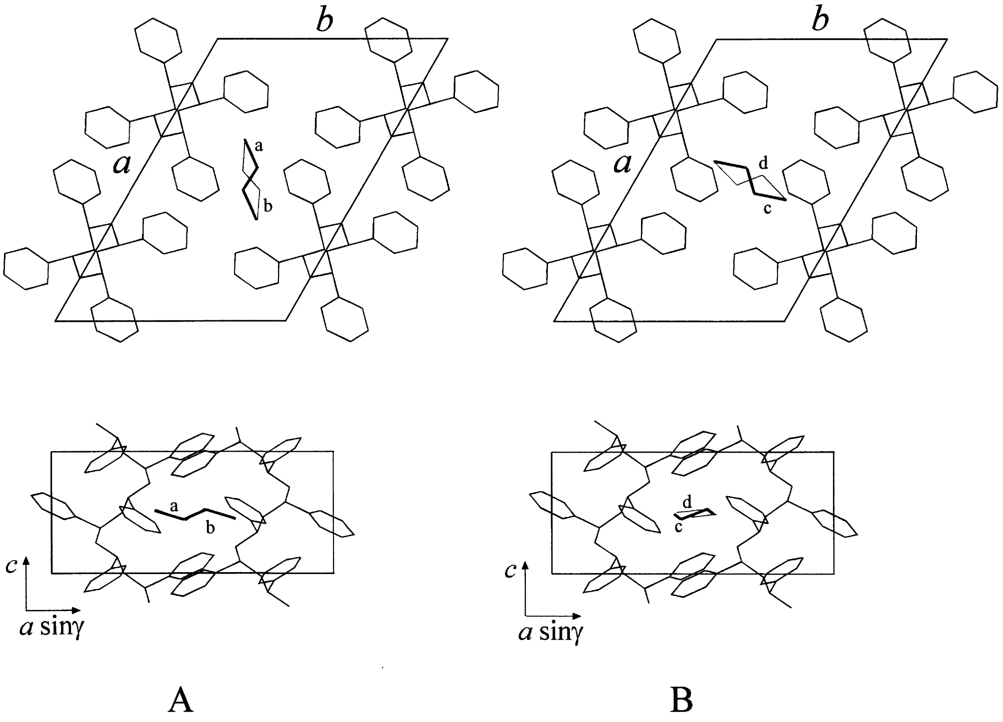

Fig. 7. *ab* and *c-asinγ* projections of the models of packing corresponding to the packing energy minima a, b (A) and c, d (B) of the maps of Fig. 6.

trans conformation, are reported in Fig. 6*A* and *B*. Only the regions of the space ω_x, ω_y, ω_z corresponding to different orientations of the guest molecule are reported. It is apparent from Fig. 6 that the maps present four regions of low energy. The energy differences between the deepest minima, indicated with a, b, c, d, are lower than 1 kJ mol^{-1}.The projections along the *c* and *b* axes of the models corresponding to the four minima (indicated by a, b, c and d) are reported in Fig. 7. It is apparent that the packing models corresponding to the minima a and b (Fig. 7*A*) and to the minima c and d (Fig. 7*B*) present the chlorine atoms of the DCE molecule in nearly the same position. Hence, if only the position of the chlorine atoms inside the cavity is considered, the four models of Fig. 7 are reduced to only two different models. Other packing models having chlorine atoms in nearly the same position can be

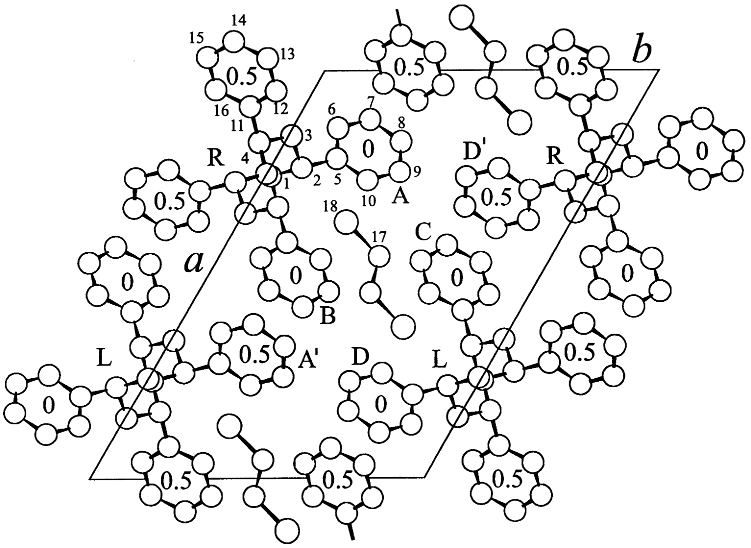

Fig. 8. Model of packing for the crystal structure of the clathrate δ form of s-PS containing DCE molecules in the space group $P2_1/a$. The atoms of the asymmetric unit (atoms 1–18) are labelled. The approximate *z* fractional coordinates of the barycentres of the phenyl rings are also shown. R = right-, L = left-handed chain. The letters A–D, A′, D′ indicate the phenyl rings which surround the DCE molecules.

Table 2
Fractional coordinates of the atoms of the asymmetric unit in the model of Fig. 8 for the clathrate δ form of s-PS with DCE in the space group $P2_1/a$. The asymmetric unit corresponds to the two monomeric units and the atoms of DCE labelled in Fig. 8

	x/a	y/b	z/c
C1	0.253	0.008	0.014
C2	0.231	0.086	0.142
C3	0.154	0.001	0.264
C4	0.170	−0.085	0.386
C5	0.208	0.175	0.047
C6	0.135	0.126	0.936
C7	0.113	0.208	0.849
C8	0.166	0.338	0.872
C9	0.240	0.387	0.983
C10	0.261	0.305	0.071
C11	0.084	−0.173	0.483
C12	0.046	−0.123	0.594
C13	−0.033	−0.203	0.682
C14	−0.074	−0.334	0.660
C15	−0.035	−0.384	0.549
C16	0.044	−0.303	0.460
C17	0.455	0.482	0.453
Cl18	0.372	0.324	0.511

obtained from corresponding points inside the minima regions of the maps of Fig. 6, taken near the points a and b, or c and d. It is worth noting that in the regions of low packing energy, the atoms of the guest DCE molecule are nearly at the same height with a maximum deviation from $z/c = 0.5$ in the 0.3-0.4 Å range.

The feasibility of the different models of packing corresponding to the different positions of the DCE molecules in the unit cell, which give the packing energy minima, has been verified by calculations of structure factors. Structure factor calculations have also been performed for models near the packing energy minima inside the large minimum regions of the maps of Fig. 6. A good agreement between calculated structure factors and the experimental intensities observed in the X-ray fibre diffraction pattern of Fig. 1 is obtained for a model corresponding to the point indicated with an asterisk in the maps of Fig. 6 ($\omega_x = 35°$, $\omega_y = 160°$, $\omega_z = 105°$), when DCE molecules are in *trans* conformation and s-PS chains positioned with $\omega = 165°$ and $z = 2.90$ Å (absolute minimum of the map of Fig. 4).

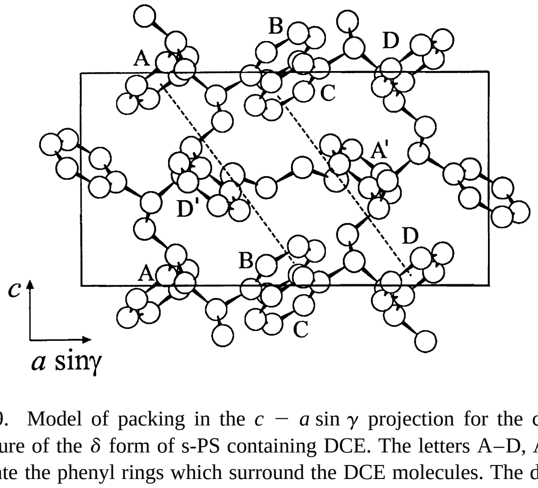

Fig. 9. Model of packing in the $c - a \sin \gamma$ projection for the crystal structure of the δ form of s-PS containing DCE. The letters A–D, A′, D′ indicate the phenyl rings which surround the DCE molecules. The dashed lines indicate that both chlorine atoms are sandwiched between the benzene rings A,B and C,D.

The model of packing of the clathrate δ form of s-PS containing DCE which gives the best agreement is shown in Fig. 8. The fractional coordinates of the carbon atoms of the asymmetric unit in the model of Fig. 8, for the space group $P2_1/a$, are listed in Table 2. The calculated and observed structure factors are compared in Table 3. A fairly good agreement is apparent: the final discrepancy factor is $R = 14\%$ for all observed reflections.

Since the X-ray scattering amplitude of chlorine is about three times larger than that of carbon, the intensities of the reflections in the X-ray fibre diffraction pattern depend on slight changes in DCE content, as well as on the presence of possible disorder in the positioning of DCE molecules inside the cavities. This can be largely responsible for the slight discrepancies present in the comparison of Table 3.

It is apparent from Fig. 8 that, between adjacent s-PS helices along the a axis, there is no open space sufficient to accommodate a DCE molecule, since right-handed and left-handed chains come into contact at the van der Waals distances (the shortest intermolecular distance between phenyl carbon atoms is 3.8 Å). On the contrary, between adjacent helices along the (a–b) direction, one molecule of DCE in the *trans* conformation can be accommodated in an isolated cavity being surrounded by 10 polymer benzene rings, as also shown in Fig. 9 where the crystal structure model is viewed along the b axis. The shortest distances between the atoms of DCE and the atoms of the polymer chains are at 3.6 Å, between the chlorine atom 18 and the methylene carbon atom (8), and at 3.4 and 3.45 Å, between carbon atom 17 and two carbon atoms of the closest benzene ring. All other distances between the atoms of the DCE molecule and the carbon atoms of the neighbouring s-PS chains are greater than 3.8 Å.

It is worth noting that both chlorine atoms of a DCE molecule are sandwiched between two benzene rings of the same s-PS chain (see Fig. 9). This particular positioning of the DCE molecule in the cavity allows the establishment of a very large number of non-bonded attractive interactions between each chlorine atom and the carbon atoms of the neighbouring s-PS chains; indeed, as many as 25 distances, all included between 3.8 and 5.0 Å, with an average distance of 4.4 Å, which give attractive interactions, are present.

Although a good agreement between calculated and observed X-ray intensities has been obtained for the proposed model of Figs 8 and 9, a better agreement could be obtained for a model characterised by a position of the chlorine atoms averaged over different positions corresponding to situations with low packing energy. Indeed, structure factor calculations have also been performed for

Table 3
Comparison between the calculated structure factors F_c for the model of the clathrate δ form with DCE of Fig. 8,‘ in the space group $P2_1/a$, and the observed structure factors F_o, evaluated from the intensities observed in the X-ray fibre diffraction pattern of Fig. 1. The Bragg distances, observed in the X-ray fibre diffraction pattern of Fig. 1 and calculated for the unit cell with axes $a = 17.11$ Å, $b = 12.17$ Å, $c = 7.7$ Å and with $\gamma = 120°$, are also shown ne = not evaluated

hkl	d_{obs}(Å)	d_{calc}(Å)	F_c		F_o
010	10.4	10.57	9.7		11.5
$\bar{2}10$	8.23	8.33	23.0		28.9
200		7.41	3.0		
$\bar{2}20$		5.91	7.9		
020	5.21	5.27	21.2	25.3	17.4
210		5.00	13.8		
$\bar{4}10$	4.23	4.22	13.0	15.2	18.4
$\bar{4}20$		4.16	7.7		
$\bar{2}30$		4.06	9.5		
$\bar{4}30$		3.60	6.2		
220	3.49	3.54	15.2	26.1	20.5
030		3.51	21.2		
410		3.05	3.6		
$\bar{2}40$		3.00	19.5		
$\bar{6}20$		2.85	4.6		
$\bar{6}30$		2.78	5.6		
$\bar{6}10$		2.73	9.0		
230	2.64	2.70	11.4	17.6	19.7
040		2.63	13.4		
$\bar{6}40$		2.55	5.0		
420		2.50	15.5		
600		2.47	5.9		
$\bar{4}50$		2.43	18.7		
$\bar{1}11$	6.45	6.45	9.7		6.2
011		6.22	5.6		
201		5.34	6.2		
111	5.07	5.21	26.8	34.3	32.1
$\bar{1}21$		4.73	18.4		
$\bar{2}21$		4.69	10.9		
$\bar{3}11$		4.58	13.8		
$\bar{3}21$	4.18	4.25	48.0	56.4	57.8
211		4.19	10.5		
301		4.16	27.7		
121	3.67	3.77	16.4	38.7	41.7
$\bar{4}11$		3.70	28.1		
$\bar{4}21$		3.66	21.0		
$\bar{2}31$		3.59	6.7		
$\bar{3}31$	3.37	3.51	11.8	25.3	18.1
$\bar{1}31$		3.47	16.4		
311		3.41	15.2		
$\bar{4}31$		3.26	4.2		
221		3.22	4.5		
$\bar{5}21$		3.12	2.1		
$\bar{5}11$		3.05	11.8		
$\bar{5}31$		2.94	19.2		
002		3.85	ne		
102		3.73	7.3		
$\bar{1}12$	3.49	3.66	17.3	33.5	24.8
012		3.62	12.2		
$\bar{2}12$		3.49	25.9		
202		3.42	1.7		
112		3.38	10.4		
$\bar{2}22$		3.23	12.6		
022	3.04	3.11	10.5	31.3	30.7
322		3.07	18.2		
212		3.05	11.8		
302		3.04	20.0		

ne = not evaluated

a statistical model characterized by DCE molecules arranged statistically in the four positions corresponding to the four packing energy minima a, b, c and d (Fig. 7). These calculations give a good agreement with the observed X-ray intensities, although not better than that obtained for the proposed model of Figs 8 and 9 (Table 3). It is, however, reasonable to assume the presence of disorder in the positioning of the DCE molecules inside the cavities.

We have also analysed the possibility that DCE molecules in the cavities could be in *gauche* conformation. Indeed, packing energy and structure factor calculations have also been performed for models of packing where the cavity contains DCE in *gauche* conformation. In this case, in the assumption that the barycentre of the C–C bond of the DCE molecule in *gauche* conformation is coincident with the centre of symmetry of the lattice, we have obtained values of the packing energy always higher than those of the model with DCE in *trans* conformation (the absolute energy minimum is $6\,\mathrm{kJ\,mol^{-1}}$ higher than the absolute minimum of Fig. 6). In any case, structure factor calculations for models with DCE molecules in *gauche* conformation, having reasonable values of the packing energy, are always in bad agreement with the observed X-ray intensities. This analysis indicates that the DCE molecules absorbed in the crystalline phase, as guest molecules in the polymeric clathrate, are essentially only in *trans* conformation. These results are in agreement with the results found by *FT*i.r. analysis [14].

4. Conclusions

The crystal structure of the clathrate δ form of s-PS containing DCE has been determined by the analysis of the X-ray fibre diffraction pattern and packing energy calculations. Chains in the helical **s**(2/1)2 conformation and DCE molecules are packed in the monoclinic unit cell with axes $a = 17.11$ Å, $b = 12.17$ Å, $c = 7.7$ Å and with $\gamma = 120°$ according to the space group $P2_1/a$; the molar ratio of monomer/DCE is 4/1. The crystalline density of the clathrate δ form is 1.23 g cm^{-3} with two chains (eight monomer units) and two DCE molecules inside the unit cell. Benzene rings of adjacent polymer chains delimit isolated cavities; each cavity is occupied by one molecule of DCE which is essentially only in the *trans* conformation.

Disorder in the positioning of the DCE molecules inside the cavities is probably present. Nevertheless, it is worth noting that the location and the conformation of DCE in the cavity, shown by the present structural analysis, is such that both chlorine atoms are sandwiched between two benzene rings of the same polymer chain. This positioning of the DCE molecules allows the establishment of a large number of attractive interactions between each chlorine atom and the carbon atoms of the neighbouring s-PS chains. This situation is not feasible for the case of the guest in the *gauche* conformation; hence, these attractive interactions can probably account for the *trans* conformation adopted by DCE molecules.

Acknowledgements

Financial support from the ‘Ministero dell’Università e della Ricerca Scientifica e Tecnologica’ is gratefully acknowledged.

References

[1] Guerra G, Vitagliano VM, De Rosa C, Petraccone V, Corradini P. Macromolecules 1990;23:1539.
[2] Chatani Y, Shimane Y, Inoue Y, Inagaki T, Ishioka T, Ijitsu T, Yukinari T. Polymer 1992;33:488.
[3] De Rosa C, Guerra G, Petraccone V, Corradini P. Polym J 1991;23:1435.
[4] De Rosa C. Macromolecules 1996;29:8460.
[5] De Rosa C, Guerra G, Corradini P. Rend Fis Acc Lincei 1991;2:227.
[6] De Rosa C, Rapacciuolo M, Guerra G, Petraccone V, Corradini P. Polymer 1992;33:1423.
[7] Chatani Y, Shimane Y, Ijitsu T, Yukinari T. Polymer 1993;34:1625.
[8] Immirzi A, De Candia F, Iannelli P, Vittoria V, Zambelli A. Makromol Chem Rapid Commun 1988;9:761.
[9] Chatani Y, Shimane Y, Inagaki T, Ijitsu T, Yukinari T, Shikuma H. Polymer 1993;34:1620.
[10] Chatani Y, Inagaki T, Shimane Y, Shikuma H. Polymer 1993;34:4841.
[11] Guerra G, Manfredi C, Rapacciuolo M, Corradini P, Mensitieri G, Del Nobile MA. Italian Patent 1994 (C.N.R.).
[12] Manfredi C, De Rosa C, Guerra G, Rapacciuolo M, Auriemma F, Corradini P. Macromol Chem Phys 1995;196:2795.
[13] De Rosa C, Guerra G, Petraccone V, Pirozzi B. Macromolecules 1997;30:4147.
[14] Guerra G, Manfredi C, Musto P, Tavone S. Macromolecules 1998;31:1329.
[15] Zambelli A, Pellecchia C, Oliva L, Longo P, Grassi A. Macromol Chem 1991;192:223.
[16] Cromer DT, Mann JB. Acta Crystallogr Sect A 1968;24:321.
[17] Yoon DY, Sundararajan PR, Flory PJ. Macromolecules 1975;8:776.
[18] Suter UW, Flory PJ. Macromolecules 1975;8:765.
[19] Brant DA, Miller WG, Flory PJ. J Mol Biol 1967;23:47.
[20] Ketelaar J. Chemical constitution. New York: Elsevier, 1958.
[21] Hopfinger AJ. Conformational properties of macromolecules. New York: Academic Press, 1979.